Appendix "B" for

Declaration of Dr. Karl Schermanz Under 37 CFR 1.132

The influence of Tungsten on SCR activity in a TiO2-Rare Earth-V- System

I, Prof. Alessandro Trovarelli, one of the inventors of WO 2005/046864, declare that I have undertaken the following experiments showing the significant influence of tungsten in the TiO2-RE-Vanadate system on NOx conversion. For this there were compared 2 tungsten free and 2 tungsten containing materials based on TiO2-RE-Vanadates (RE being Er and Tb).

A) **Preparation of the Tungsten free materials:**

Preparation of TiO2/ 8.41% $ErVO_4$

104.6 mg of ammonium metavanadate were dissolved in 15 ml of oxalic acid 1N. The solution was heated in order to obtain the blue complex $(NH_4)_2[VO(C_2O_4)_2]$ and then 3717.17 mg of Er-acetate solution were added. Moreover, some drops of HNO_3 were added in order to avoid the precipitation of the terbium oxalate. Then, the support [2747.7 mg of TiO_2 (DT 51)] was added. This slurry was brought to dryness under continuous stirring at 80-100°C. Finally, the solid was dried at 120°C overnight and calcined at 650°C for 2 hours, pressed into pellets, crushed and sieved in the range 355-425 µm. Ageing of the sample was carried out in a tubular furnace at a temperature of 750°C for 10 h under air.

Preparation of TiO2/ 8.41% $TbVO_4$

107.7 mg of ammonium metavanadate were dissolved in 15 ml of oxalic acid 1N. The solution was heated in order to obtain the blue complex $(NH_4)_2[VO(C_2O_4)_2]$ and then 417.3 mg of $Tb(NO_3)_3 \cdot 6H_2O$ were added. Moreover, some drops of HNO_3 were added in order to avoid the precipitation of the terbium oxalate. Then, the support [2747.7 mg of TiO_2 (DT 51)] was added. This slurry was brought to dryness under continuous stirring at 80-100°C. Finally, the solid was dried at 120°C overnight and calcined at 650°C for 2 hours, pressed into pellets, crushed and sieved in the range 355-425 µm. Ageing of the sample was carried out in a tubular furnace at a temperature of 750°C for 10 h under air.

B) Preparation of Tungsten containing materials:

Preparation of TiO2/WO3/ 8.41% $ErVO_4$ (corresponds to 5 % Er and 1,5 % V)

This material was prepared accoding to example 17 of WO 05/046864.

Preparation of TiO2/ 8.41% $TbVO_4$

This material was prepared accoding to example 18 of WO 05/046864.

Catalyst testing was carried out in the apparatus described in WO 05/046864. The gas feed consisted of NH_3/N_2, NO/N_2, O_2, N_2. Mass flow meters were used to measure and control the single gaseous stream while an injection pump was used to introduce water. The feed stream was preheated and premixed and ammonia was added to the gaseous mixture immediately before entering the reactor to avoid side reactions. A tubular quartz reactor was employed inserted in a furnace. Temperature was controlled by a thermocouple inserted in the catalyst bed. The gas exiting the reactor was scrubbed with an aqueous solution of phosphoric acid to trap unconverted ammonia and then cooled to condense water vapor. Activity of the catalysts were measured under stationary conditions in a temperature range of 250°C to 450°C. Unless otherwise reported the standard gas composition and reaction conditions given in Table 1 were used. Conditions were selected in order to have a conversion not exceeding ca. 90% with reference catalyst. Gas composition analysis was carried out with an FTIR spectrometer equipped with a gas cell.

Results and conclusion:

The tungsten free catalysts show significant lower activity and particularly a drop in catalytic activity after thermal treatments, in contrast to what was found for the WO3 containing materials (compare examples 17, 17a and 18, 18a in table 2 and Table 3).

These results clearly show that WO_3 plays a significant role in increasing the activity and thermal stability of these catalysts.

Table 1: Reaction conditions and gas composition.

Catalyst weight	100,0 mg
Particle size	350-425 µm
Total flow	0,3 l/min
Temperature	250-450°C
NO conc.	200 ppm
NH3 conc.	240 ppm
O2 conc.	20000 ppm
H2O conc.	10%
N2 conc.	balance

Table 2: Activity (NOx conversion in %) of tungsten free catalysts, fresh and aged catalysts containing RE and V and TiO2.

Example Nr	RE	RE [%]	V [%]	250°C fresh	320°C fresh	450°C fresh	250°C aged	320°C aged	450°C aged
17a	Er	4,6	1,7	31	66	20	0	9	6
18a	Tb	4,6	1,7	28	60	21	10	21	0

Table 3: Activity (NOx conversion in %) of tungsten containing catalysts, fresh and aged catalysts containing RE and V and WO3 and TiO2 (WO3 : TiO2 =10:90).

Example Nr	RE	RE [%]	V [%]	250°C fresh	320°C fresh	450°C fresh	250°C aged	320°C aged	450°C aged
17	Er	4,6	1,7	58	81	46	17	46	9
18	Tb	4,6	1,7	62	88	48	25	48	29

Prof. Alessandro Trovarelli